

# STABILITY FIELD AND THERMAL EQUATION OF STATE OF $\epsilon$ -IRON DETERMINED BY SYNCHROTRON X-RAY DIFFRACTION IN A MULTIANVIL APPARATUS

High-pressure x-ray diffraction data on pure  $\epsilon$ -iron at various temperatures have been measured. The inferred equation of state allowed estimation of the density of pure iron under the pressure and temperature conditions present at the Earth's core. This estimated density is higher than that indicated for the Earth's core by seismological data, supporting the notion that light element(s) must be present in the inner core as well as the outer core of the Earth.

The Earth's core consists of a liquid outer core and a solid inner core [1] that are believed to be made predominantly of iron (Fe) [2,3]. The crystal structure, melting temperature, and equation of state (EOS) of Fe, therefore, provide important clues to infer the composition and the thermodynamic state of the core. In the present study, we use a "T-cup" multianvil apparatus combined with the synchrotron x-rays at the Advanced Photon Source (APS) to establish the stability field and EOS of  $\epsilon$ -Fe up to 20 GPa and 1500 K. The stability field of Fe is characterized by the location of the  $\alpha$ - $\epsilon$ - $\gamma$  triple point and the  $\epsilon$ - $\gamma$  boundary. The pressure-volume-temperature ( $P$ - $V$ - $T$ ) data set obtained for  $\epsilon$ -Fe is fitted to several high-temperature EOSs. The accuracy of our data allows us to examine structural distortion (represented by the  $c/a$  ratio) as a function of  $P$  and  $T$ . The density of  $\epsilon$ -Fe is then calculated from the EOS of pure  $\epsilon$ -Fe at the Earth's core conditions. Comparison to the density from the preliminary reference Earth model (PREM) provides constraints on the possible presence of light element(s) in the Earth's core.

High  $P$  and  $T$  *in situ* x-ray diffraction experiments were performed using the 250-ton press installed at the GSECARS 13-BM-D beamline at the APS, with a double-stage split-cylinder "T-cup" apparatus. Diffraction patterns were collected based on the energy dispersive method with an energy range

of 20 to 100 keV. Incident x-ray beam size was  $100 \times 300 \mu\text{m}$ . Diffracted x-rays were detected by a Ge solid-state detector at a fixed diffraction angle of  $6^\circ$ .

Both polycrystalline Fe and pressure calibrant Au were mixed with MgO to inhibit grain growth. Temperature was monitored by a  $\text{W}_{0.94}\text{Re}_{0.06}$ - $\text{W}_{0.75}\text{Re}_{0.25}$  thermocouple. Pressure was determined from the Au diffraction lines based on the high  $P$  and  $T$  EOS of Au [4].

The experiment consisted of two runs: one clarified the phase relations and the other collected  $P$ - $V$ - $T$  data of  $\epsilon$ -Fe. Our criterion for determining the phase boundary is as follows. A diffraction profile was taken from the sample first, followed by the diffraction pattern of Au to determine the pressure. Then the sample x-ray pattern was collected again without changing  $P$  and  $T$ . This procedure tests the kinetics of the transition, so comparison of two patterns before and after pressure determination (typical time interval is 6 min) clarifies the stable phase, whose diffraction intensity should grow. To extract EOS parameters,  $P$ - $V$ - $T$  data were collected only in the  $\epsilon$  phase stability field to avoid peak overlap. The maximum temperature was kept at 1000 K. Diffraction lines of the  $111$ ,  $200$ ,  $220$ ,  $311$ , and  $222$  peaks from Au were used to determine pressure [4], and the  $100$ ,  $002$ ,  $101$ ,  $110$ , and  $103$  lines of the  $\epsilon$ -Fe were used to obtain cell volumes throughout the experiment.

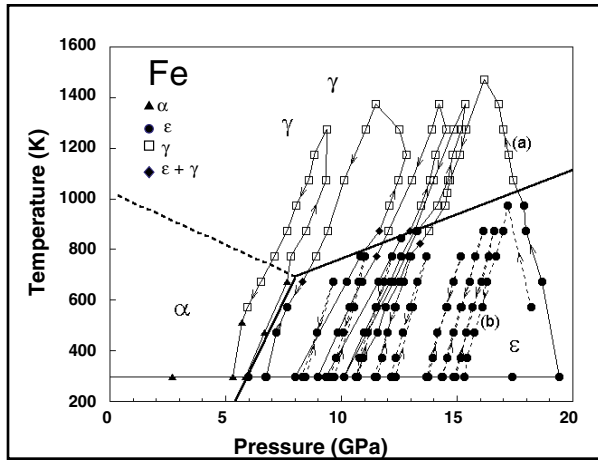


FIG. 1. Phase diagram of Fe determined by in situ x-ray observation, together with experimental P-T paths. Triangles, circles, squares represent which phase of  $\alpha$ ,  $\epsilon$ , and  $\gamma$  is dominant under corresponding P and T conditions. Diamonds represent the data points where the dominant phase is inconclusive because of little time dependence of diffraction peaks. Thin solid and dashed lines indicate (a) first run (#T0105) to see the phase boundary and (b) second run (#T0134) for P-V-T measurement of  $\epsilon$ -Fe, respectively. Arrows show directions of the P-T path. Temperature fluctuation was only about 5 K at 1500 K.

Transformation boundaries between the  $\epsilon$  and  $\gamma$  phases determined by this method are shown in Fig. 1. Our data indicate that the triple point of  $\alpha$ ,  $\epsilon$ , and  $\gamma$  phases of Fe is located at 8.0(3) GPa and 680(50) K, which is close to that determined by a previous study using a cubic-anvil high-pressure apparatus (8.3 GPa and 713 K) [5] after carefully taking into account the effects of time dependence due to transition kinetics by repeating heating and cooling cycles. The slope of the  $\epsilon$ - $\gamma$  boundary is 36(3) K/GPa<sup>-1</sup>, which is steeper than that in one diamond anvil cell (DAC) experiment (24 K/GPa<sup>-1</sup>) [6] but is in excellent agreement with the results obtained by cubic-anvil press (34 K/GPa<sup>-1</sup>; as estimated from their Fig. 2) [5] and another DAC result (35 K/GPa<sup>-1</sup>) [7].

Combined with data in the DAC, room temperature volume data yield a third-order Birch-Murnaghan EOS with  $K_0 = 135(19)$  GPa,  $K'_0 = 6.0(4)$ , and  $V_0 = 22.7(3)$  Å<sup>3</sup> [3]. A total of 55 data points collected during cooling cycles are fit to several high- $T$  EOSs. The fit to the Mie-Grüneisen-Debye EOS yields the Debye temperature, Grüneisen parameter, and the parameter  $q$  to be 998(85) K, 1.36(8), and

0.91(7), respectively. The Mie-Grüneisen-Debye EOS, high-temperature Birch-Murnaghan EOS, and thermal pressure approach based on Mie-Grüneisen theory are all consistent in the current  $P$  and  $T$  range, but the Mie-Grüneisen-Debye EOS yields the best fit (Fig. 2).

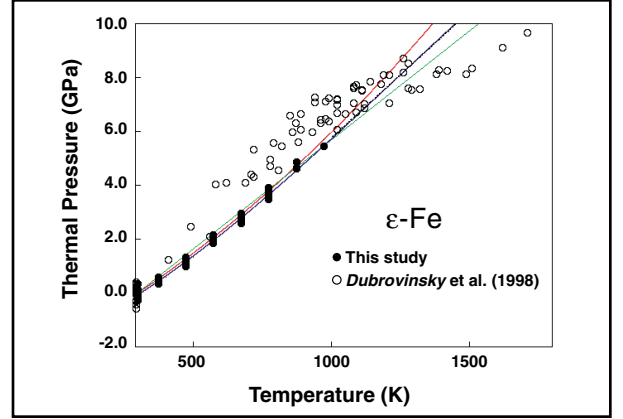


FIG. 2. Thermal pressure of  $\epsilon$ -Fe up to 20 GPa and 1000 K, together with previous work [8]. The 55 cooling cycle data points are fitted to Anderson's thermal pressure approach with (red line) and without the  $(\partial^2 P / \partial T^2)$  term (solid line) and Mie-Grüneisen-Debye approach (blue line). The best fit to our data is Mie-Grüneisen-Debye equations within this temperature range. Above the Debye temperature of 998 K, the blue line shows the extrapolation based on linear function.

The  $c/a$  ratio increases with  $T$  and decreases slightly with  $P$  (Fig. 3). The room-temperature  $c/a$

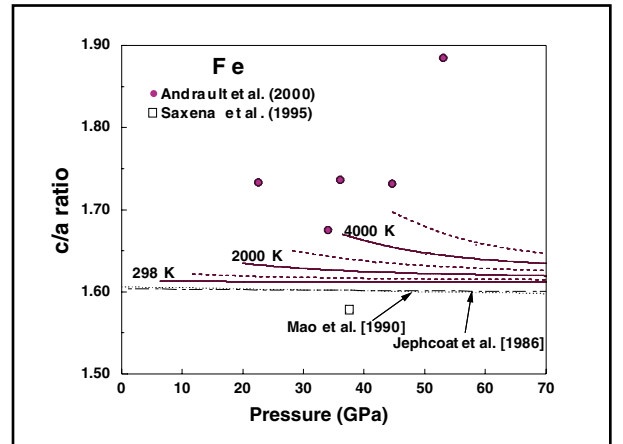


FIG. 3. Comparison of  $c/a$  ratio as a function of  $P$  and  $T$ . Solid circles and open square shows the pseudo  $c/a$  of the orthorhombic phase [12] and the  $c/a$  of the dhcp phase [13], respectively. Solid lines (298, 2000, and 4000 K) and dashed lines (1000, 3000, and 5000 K) show extrapolations of the present study. Room temperature  $c/a$  variations as a function of pressure [9, 10] are also plotted.

ratio of  $\epsilon$ -Fe is reported to decrease as a function of pressure:  $c/a = 1.606(1) - 1.2(3) \times 10^{-4}P$  (GPa) [9];  $c/a = 1.604(2) - 0.49(14) \times 10^{-4}P$  (GPa) [10]. Our room-temperature  $c/a$  is represented by  $c/a = 1.613 - 1.6 \times 10^{-6}P$  (GPa) as a linear function, which is 0.4 to 0.8% larger than that at pressures up to 200 GPa [9]. The pressure dependence of  $c/a$  is still smaller than that reported by Mao et al. [10] by one order of magnitude. From the scatter of the data in these studies, however, a 0.4 to 0.8% difference in  $c/a$  should be regarded as experimental error. The  $c/a$  ratio does not support the possibility of phase transition up to the Earth's core condition.

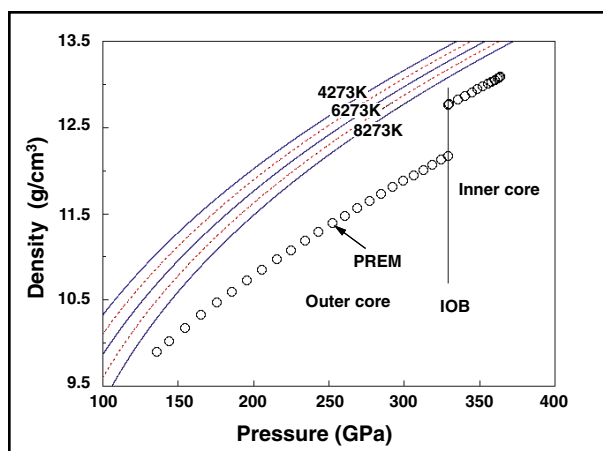


FIG. 4. Density of  $\epsilon$ -Fe at the Earth's core condition. Blue solid and red dotted lines are obtained by extrapolation of Mie-Grüneisen-Debye EOS. Solid lines indicate 4273, 6273, and 8273 K and dotted lines 5273, and 7273 K, respectively. Circles are PREM densities. The  $\epsilon$ -Fe densities are significantly higher than those for PREM, supporting the existence of light element(s) in both the inner and outer core.

On the assumption that the inner core is composed of pure  $\epsilon$ -Fe, extrapolation of Mie-Grüneisen-Debye EOS allows us to estimate the density under the Earth's core condition. Figure 4 shows the density of  $\epsilon$ -Fe as a function of pressure along several isotherms, together with the density of PREM [1]. In order for the density of pure  $\epsilon$ -Fe to match that of

PREM, core temperatures must be exceedingly high. Even when the highest available estimate of an inner-core boundary (ICB) temperature of 7600 K [11] is employed,  $\epsilon$ -Fe still has about 4% excess density compared to PREM. This result supports the notion that light element(s) must be present in the inner core, as well as the outer core [14].

Principal publication: "Stability Field and Thermal Equation of State of  $\epsilon$ -Iron Determined by Synchrotron X-ray Diffraction in a Multi-anvil Apparatus," J. Geophys. Res. **106**, 21799-21810 (2001).

## REFERENCES

- [1] A.M. Dziewonski and D.L. Anderson, Phys. Earth Planet. Inter. **25**, 297-356 (1981).
- [2] F. Birch, J. Geophys. Res. **57**, 227-286 (1952).
- [3] F. Birch, J. Geophys. Res. **69**, 4377-4388 (1964).
- [4] O.L. Anderson, D.G. Isaak, and S. Yamamoto, J. Appl. Phys. **65**, 1534-1543 (1989).
- [5] S. Akimoto, T. Suzuki, T. Yagi, and O. Shimomura, in *High Pressure Research in Mineral Physics*, Geophys. Monogr. Ser., vol. 39, edited by M.H. Manghnani and Y. Syono (TERRAPUB/AGU, Tokyo, 1987), pp. 149-154.
- [6] R. Boehler, M. Nicol, and M.L. Johnson, in *High Pressure Research in Mineral Physics*, Geophys. Monogr. Ser., vol. 39, edited by M.H. Manghnani and Y. Syono (TERRAPUB/AGU, Tokyo, 1987), pp. 173-176.
- [7] H.-K. Mao, P.M. Bell, and C. Hadidiacos, in *High Pressure Research in Mineral Physics*, Geophys. Monogr. Ser., vol. 39, edited by M.H. Manghnani and Y. Syono (TERRAPUB/AGU, Tokyo, 1987), pp. 135-138.
- [8] L.S. Dubrovinsky, S.K. Saxena, and P. Lazor, Phys. Chem. Mineral **25**, 434-441 (1998).
- [9] A.P. Jephcoat, H.-K. Mao, and P.M. Bell, J. Geophys. Res. **91**, 4677-4684 (1986).
- [10] H.-K. Mao, Y. Wu, L.C. Chen, J.F. Shu, and A.P. Jephcoat, J. Geophys. Res. **95**, 21,737-21,742, (1990).
- [11] Q. Williams, R. Jeanloz, J. Bass, B. Svendsen, and T. J. Ahrens, Science **236**, 181-182 (1987).
- [12] D. Andrault, G. Fiquet, T. Charpin, and T. le Bihan, Am. Mineral. **85**, 364-371 (2000).
- [13] S.K. Saxena, L.S. Dubrovinsky, P. Häggkvist, Y. Cerenius, G. Shen, and H.K. Mao, Science **269**, 1703-1704 (1995).
- [14] A.P. Jephcoat and P. Olsen, Nature **325**, 332-335, (1987).

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